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Pyrolysis-catalytic steam reforming of agricultural biomass wastes and biomass components for production of hydrogen/syngas

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ABSTRACT

The pyrolysis-catalytic steam reforming of six agricultural biomass waste samples as well as the three main components of biomass was investigated in a two stage fixed bed reactor. Pyrolysis of the biomass took place in the first stage followed by catalytic steam reforming of the evolved pyrolysis gases in the second stage catalytic reactor. The waste biomass samples were, rice husk, coconut shell, sugarcane bagasse, palm kernel shell, cotton stalk and wheat straw and the biomass components were, cellulose, hemicellulose (xylan) and lignin. The catalyst used for steam reforming was a 10 wt.% nickel-based alumina catalyst ($NiAl_2O_3$). In addition, the thermal decomposition characteristics of the biomass wastes and biomass components were also determined using thermogravimetric analysis (TGA). The TGA results showed distinct peaks for the individual biomass components, which were also evident in the biomass waste samples reflecting the existence of the main biomass components in the biomass wastes. The results for the two-stage pyrolysis-catalytic steam reforming showed that introduction of steam and catalyst into the pyrolysis-catalytic steam reforming process significantly increased gas yield and syngas production notably hydrogen. For instance, hydrogen composition increased from 6.62 to 25.35 mmol g^{-1} by introducing steam and catalyst into the pyrolysis-catalytic steam reforming of palm kernel shell. Lignin produced the most hydrogen compared to cellulose and hemicellulose at 25.25 mmol g^{-1}. The highest residual char production was observed with lignin which produced about 45 wt.% char, more than twice that of cellulose and hemicellulose.

1. Introduction

Energy demand around the world have progressively been increasing due to population growth and increased economic development. The desire for the production of energy from renewable sources rather than fossil fuels has been stimulated by concerns over global warming linked to greenhouse gas emissions from fossil fuel use and issues of sustainability [1,2]. Biomass, as a source of energy, has received great interest, because it is a sustainable and renewable source of energy with several readily available feedstocks of biomass wastes from agricultural residues, forestry residues, municipal solid waste, demolition and construction activities etc. Biomass resources may be classified into five categories [3,4]: (i) Virgin wood waste such as wood chips, sawdust, tree branches etc.; (ii) Energy crops grown for the purpose of energy applications such as jatropha, pongamai, hybrid eucalyptus, napier grass and miscanthus; (iii) Agricultural residues such as sugarcane bagasse, coconut shell, corn husks, palm kernel shells; (iv) Municipal solid waste (MSW), animal wastes and food waste; (v) Industrial waste from the manufacturing industrial processes such as construction, demolition activities [3,4].

Hydrogen is an energy carrier which is predicted to be in high demand in the future since it possesses high energy density (122 kJ kg^{-1}), which is approximately 2.75 times more than hydrocarbon fuels. Also, the combustion of hydrogen does not generate any harmful emissions and only water is produced [5,6]. Hydrogen is mainly (~95%) produced from fossil fuel coal, natural gas, and crude oil [5]. Therefore, there has been increasing interest in producing hydrogen from alternative, sustainable sources such as biomass.

One such route for hydrogen production from biomass is the two-stage pyrolysis-catalytic steam reforming process. The process mimics the natural gas catalytic steam reforming process, but the first stage pyrolysis produces a suite of hydrocarbon gases for subsequent

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reforming, rather than the hydrocarbons found in natural gas (mostly methane) [7–9]. Table 1 shows the main reactions taking place during the pyrolysis and the catalytic steam reforming/gasification process [10,11]. Pyrolysis thermally degrades the biomass to produce a range of hydrocarbons and carbonaceous species (Equation (1)). Catalytic steam reforming of the hydrocarbons, oxygenated hydrocarbons and tar produced from pyrolysis is the main process for hydrogen enriched syngas (H_2 and CO) production (Equations (2) and (3)). However, many other reactions will occur in the catalytic steam reforming reactor, including, catalytic cracking of tar, hydrocarbons and oxygenated hydrocarbons, dry (CO_2) reforming of hydrocarbons and oxygenated hydrocarbons, water gas shift reaction, char gasification etc (Equations 4–9). The two-stage pyrolysis-catalytic steam reforming reactor system has been used to effectively produce high yield hydrogen syngas. The two-stage reaction system has advantages over a single stage reactor where the biomass and catalyst are mixed together, in that there is more effective separate control of the process conditions of the pyrolysis and catalyst stages, e.g. temperature, steam input etc. [12].

Several different catalysts and catalyst support materials have been investigated for the production of hydrogen-rich syngas from the catalytic steam reforming of biomass. Platinum, palladium and rhodium metal-based catalysts have been shown to be effective for enhancing the production of hydrogen from the catalytic steam reforming/gasification of biomass [13–15]. However, such noble metal catalysts tend to be expensive. Lower cost transition metals such as nickel have been used as the preferred nickel-based catalysts used in the commercial natural gas catalytic steam reforming process for industrial scale hydrogen production. Therefore, nickel based catalysts have also been investigated for the pyrolysis-catalytic steam reforming of biomass for hydrogen production and have been shown to be effective [12,16]. Different support materials for the nickel metal have also been investigated to maximise the production of hydrogen, for example, Al_2O_3, SiO_2, dolomite, zeolites and MCM-41 [12,17–20]. Alumina (Al_2O_3) is a common support material used for hydrogen production via catalytic steam reforming due to its chemical and physical stability, high mechanical resistance and high nickel particle dispersion throughout the Al_2O_3 material [21]. High volumetric concentrations of hydrogen can be achieved through the pyrolysis-catalytic steam reforming of biomass at more than 50 vol% [12].

The two-stage pyrolysis-catalytic steam reforming process for biomass, involves the evolution of hydrocarbons from the biomass during the pyrolysis process which then become subsequently reformed in the catalytic steam reactor. Biomass is composed of mainly cellulose, hemicellulose and lignin and it has been suggested that pyrolysis of biomass can be considered as the superposition of these three main components [22]. Each of the components thermally decompose to produce different inorganic and hydrocarbon gases and higher molecular weight chemical vapours which enter the catalytic steam reforming process. The volatile thermal degradation products from the pyrolysis of cellulose, include, CO, CO_2, H_2, levoglucosan, aldehydes, ketones, organic acids etc. [22,23]. Specific compounds produced from the pyrolysis of cellulose have been identified by Quan et al. [24] and include, light oxygenated species, such as, 6-acetyl-β-D-mannose, 1,4:3,6-dianhydro-a-D-glucopyranose, 3-methyl-1,2-cyclopentanedione and 5-methyl-furfural. Hemicellulose pyrolysis produces CO, CO_2, H_2, C_1—C_2 hydrocarbons, organic acids and aldehydes, specific compounds include mainly, 2-methyliminoperhydro-1,3-oxazine, tetrahydropyridazine-3,6-dione, furfural and levoglucosenone [24]. Lignin pyrolysis produces mainly, CO, C_1—C_2 hydrocarbons, phenols, organic acids, alcohols and ketones [22,23], with specific compounds identified as methylphenol, creosol, 2-methoxy-4-vinylphenol and phenanthrene [24].

This study investigates the production of hydrogen and syngas produced from the two-stage pyrolysis-catalytic steam reforming of several different agricultural waste biomass samples and the three main components of biomass. The catalyst used was 10 wt.% nickel supported on alumina (Al_2O_3). In addition, the main components of biomass, and their mixtures, were also investigated for hydrogen production using the pyrolysis-catalytic steam reforming process. Understanding the yield of product gases from different types of biomass waste will aid the optimisation of an industrial scale process for hydrogen production from an alternative non-fossil fuel source. Also, knowledge of the influence of each of the main components of biomass on hydrogen production will enhance the understanding of the processes involved.

2. Materials and methods

2.1. Materials

Six different agricultural waste biomass samples were investigated consisting of coconut shell, rice husk, sugarcane bagasse, cotton stalk, wheat straw and palm kernel shell. The three main biomass components, cellulose, hemicellulose (xylan) and lignin were obtained from Sigma-Aldrich, UK Ltd. Proximate analysis of the samples was determined using thermogravimetric analysis (TGA) using a Shimadzu TGA-50 instrument and elemental analysis was conducted using a Thermo EA2000 analyser. The results are shown in Tables 2 and 3. The highest carbon content as well as the highest fixed carbon content was exhibited by lignin. In addition, lignin exhibited a significant sulphur content. Among all the biomass samples analysed, rice husk exhibited the highest ash content which has been attributed to the high content of silica in rice husks [25].

Table 1
The main reactions of the pyrolysis-catalytic steam reforming of biomass.

Equation	Reaction
$Biomass \rightarrow H_2O + H_2 + CO + CO_2 + tar + hydrocarbon\ volatiles + char$	(1) Pyrolysis
$C_xH_yO_z + H_2O \rightarrow CO + H_2$	(2) Tar steam reforming
$C_mH_n + H_2O \rightarrow CO + H_2$	(3) Hydrocarbon volatiles steam reforming
$Tars \rightarrow H_2O + H_2 + CO + CO_2 + CH_4 + C_mH_n + C_xH_yO_z$	(4) Catalytic cracking
$C_xH_yO_z + CO_2 \rightarrow CO + H_2$	(5) Tar dry (CO_2) reforming
$C_mH_n + CO_2 \rightarrow CO + H_2$	(6) Hydrocarbon volatiles dry (CO_2) reforming
$CO + H_2O \rightarrow CO_2 + H_2$	(7) Water gas shift
$C + H_2O \rightarrow CO + CO_2 + H_2$	(8) Char steam gasification
$C + CO_2 \rightarrow 2CO$	(9) Char CO_2 gasification

Table 2
Proximate analysis of biomass samples and biomass components.

Biomass sample	Moisture	Volatile	Fixed carbon	Ash
	wt.%	wt.%	wt.%	wt.%
Coconut shell	7.16	68.58	22.00	2.26
Cotton stalk	7.33	69.54	19.47	3.67
Palm kernel shell	6.70	67.52	22.13	3.65
Rice Husk	8.02	61.43	12.53	18.02
Sugarcane	5.33	83.39	7.79	3.49
Wheat straw	5.19	64.24	15.60	14.97
Cellulose	4.74	84.16	9.85	1.25
Xylan	3.33	82.18	12.15	2.34
Lignin	3.39	57.54	34.06	5.01

The catalyst used for the catalytic steam reforming experiments was a 10 wt.% $NiAl_2O_3$ catalyst prepared by an incipient wetness method. The preparation process used an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ which was dissolved in 20 ml of deionised water and stirred under heat. The alumina (Al_2O_3) support was added to the mixture, continuously stirred, heated to 90 °C and left for 1 h until a semi-solid slurry was formed. The precursor slurry was dried overnight at 105 °C. The prepared catalyst was calcined under an air atmosphere at a temperature of 750 °C for 3 h. The catalyst was finally ground and sieved to a particle size of 50–212 μm. The BET (Brunauer, Emmet and Teller) surface area, pore size and pore volume of the fresh catalyst was determined with a NOVA 2200e surface area and pore size analyser. The BET surface area for the 10%$NiAl_2O_3$ catalyst was 127 $m^2\ g^{-1}$.

2.2. Two-stage fixed bed reactor system

The pyrolysis-catalytic steam reforming of the biomass samples was carried out using a two stage fixed bed reactor system as shown in Fig. 1. The reactor was constructed of stainless steel of 250 mm length × 30 mm internal diameter and heated externally using two separate 1.2 kW electrically heated and controlled tube furnaces. Pyrolysis of the biomass samples took place in the first stage reactor where the 2 g of feedstock was suspended in a crucible boat in the centre of the pyrolysis reactor. The second stage catalytic steam reforming reactor contained 1.0 g of the 10 wt.% $NiAl_2O_3$ catalyst held in place using stainless steel mesh and quartz wool. Uncatalysed experiments were also carried out for comparison with the catalysed steam reforming, where clean quartz sand was used in place of the catalyst in the second stage reactor. The pyrolysis temperature was 550 °C with a heating rate from ambient to 550 °C of 20 °C min^{-1}. The volatiles from the biomass pyrolysis were passed to the second stage which was preheated to catalytic bed temperature of 750 °C. Water was injected at a flow rate 5.7 g h^{-1} into the second stage catalyst bed reactor to produce steam for catalytic steam reforming. Nitrogen was used as the carrier gas at a flow rate of 200 ml min^{-1}. Thermocouples were used to monitor and control the temperatures of the biomass pyrolysis and catalyst bed. Condensers were used to collect any liquid produced via air-cooled and solid dry-ice (CO_2) cooled condensers. After the condensers, all of the non-condensable gases were collected in a 25 l Tedlar gas sample bag. The experimental procedure was to first heat the second stage catalyst reactor to 750 °C. Once the catalyst reactor temperature had stabilised, the pyrolysis reactor containing the biomass was then heated to 550 °C at a heating rate of 20 °C min^{-1}, with the addition of water injection into the second stage reactor for catalytic steam reforming of the evolved biomass pyrolysis gases. All experiments were repeated for accuracy with negligible differences between the repeated experiments. Results were the average of the repeated experiments.

2.3. Gas analysis

The gaseous products collected in the Tedlar gas sample bag were analysed immediately after each pyrolysis-catalytic steam reforming experiment using packed column gas chromatography (GC). Permanent gases, CO, H_2, N_2 and O_2, were analysed by a Varian CP 3330 GC equipped with a thermal conductivity detector (TCD), GC column of 2 m length × 2 mm diameter with a 60–80 mesh molecular sieve size HayeSep packing and Ar carrier gas. CO_2 was analysed with another Varian CP 3330 GC also equipped with thermal conductivity detector (TCD) and a 2 m long × 2 mm diameter GC column with 60–80 mesh molecular sieve and Ar as the carrier gas. Hydrocarbon gases of C_1–C_4 were determined by a third Varian CP 3380 GC with a flame ionisation detector (FID), 2 m long × 2 mm diameter GC column, 80–100 mesh HayeSep packed column and nitrogen N_2 as carrier gas.

3. Results and discussion

3.1. Characterisation of samples

The biomass samples and biomass components were characterised with thermogravimetric analysis (TGA) for the determination of the characteristics of the thermal degradation of the samples. Fig. 2 shows the TGA and the differential weight loss (DTG) thermograms of the individual biomass samples and the three main biomass components. In addition, the main components of the biomass, cellulose, hemicellulose and lignin were mixed and characterised by TGA to determine any interaction between components during the thermal degradation process. The results are shown in Fig. 3.

The TGA and DTG thermograms for the cellulose, hemicellulose and lignin are shown in Fig. 2(a) and (b) respectively. Xylan, which is a representative of hemicellulose, decomposed between temperatures of 200–350 °C, cellulose decomposition was between 350 and 400 °C while that of lignin showed a wider decomposition temperature which started at about 250 °C and continued up to about 500 °C. Liu et al. [26], studied the thermal degradation of biomass components and reported that the mass loss temperature range of hemicellulose to be

Table 3
Elemental analysis of biomass samples and biomass components.

Biomass sample	C	H	N	S	O[b]
	wt.%	wt.%	wt.%	wt.%	wt.%
Coconut shell	48.32	5.26	0.29	nd[a]	46.14
Cotton stalk	43.10	6.24	1.59	nd	49.07
Palm kernel shell	50.11	6.24	1.50	nd	42.16
Rice Husk	37.60	5.26	1.69	nd	55.45
Wheat straw	40.58	4.84	0.74	nd	53.84
Sugarcane	44.34	5.92	0.57	nd	49.17
Cellulose	41.61	5.63	0.11	nd	52.64
Xylan	42.01	6.01	Nd	nd	51.98
Lignin	60.08	5.48	1.10	1.20	32.14

[a] nd = not detected.
[b] calculated by difference.

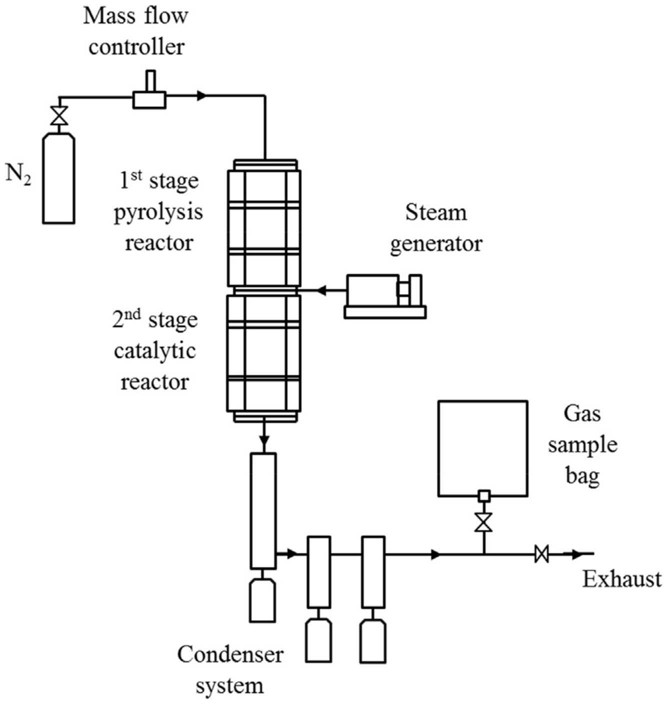

Fig. 1. Schematic diagram of the two-stage fixed bed pyrolysis-catalytic steam reforming reactor system.

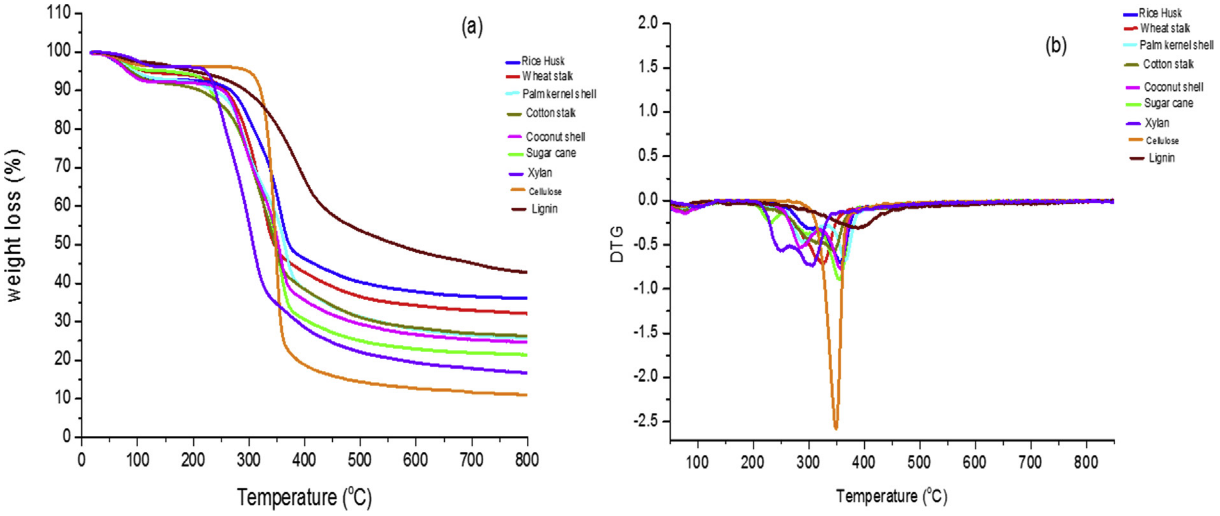

Fig. 2. (a) TGA and (b) DTG thermograms of biomass samples and the main biomass components.

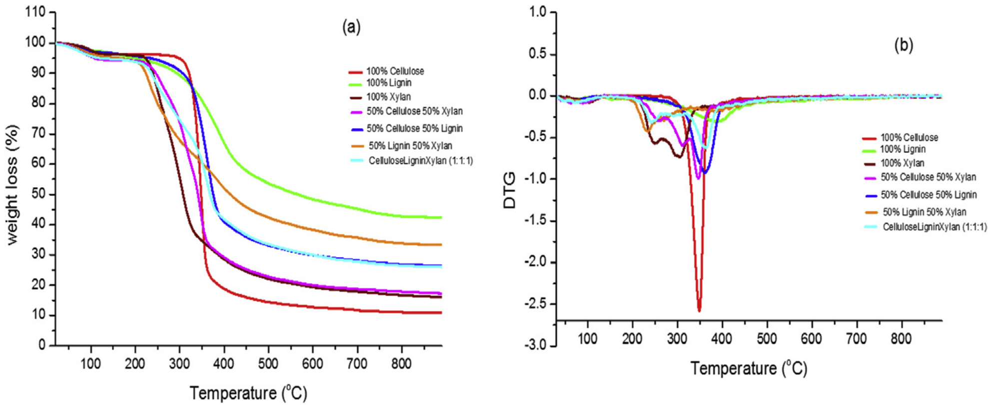

Fig. 3. (a) TGA and (b) DTG thermograms of the main biomass components and their mixtures.

between 200 and 327 °C, that of cellulose ranges between 327 and 450 °C while that of lignin ranges between 200 and 550 °C, in agreement with this study. It has been reported [22,27], that lignin is an aromatic polymer with three-dimensional linkages in an alkyl-benzene structure, and is very stable and more difficult to decompose compared to cellulose and hemicellulose, degrading over a wide temperature range. Hemicelluloses are branched polysaccharides that consist of a group of biopolymers which are more complicated than cellulose, and are reported to be thermally unstable and degrade at a lower temperature compared to cellulose and lignin [28]. Cellulose is a polysaccharide consisting of a linear polymer of $\beta(1 \rightarrow 4)$ linked D-glucose units which decomposes between 325 and 400 °C [29].

The agricultural waste biomass samples in this study may be linked to the thermal decomposition of the cellulose, hemicellulose and lignin [22,23,29–31]. The mass loss thermograms of all the agricultural waste biomass samples were between the range of the three biomass components. The thermal decomposition (TGA) of the six waste biomass samples started at ~200 °C and the DTG thermograms showed more than one peak for all the biomass samples indicating the presence and a reflection of these main biomass components as seen in Fig. 2(a) and (b). The DTG thermogram for wheat straw showed one major DTG peak at about 330 °C which suggested a composition of mainly cellulose and less of hemicellulose. Sugarcane bagasse showed three DTG peaks, at temperatures of 240, 300 and 360 °C, with the major peak where cellulose decomposition is indicated, suggesting that sugarcane bagasse contains mainly cellulose and hemicellulose. Varhegyi et al. [32] also observed three peaks for sugarcane bagasse, reporting that the first two DTG peaks could be attributed to hemicellulose and the third peak attributed to cellulose. Thermal decomposition of rice husks showed two DTG peaks at temperatures of 300 and 360 °C, with the major peak linked to cellulose and hemicellulose, and with the presence of some lignin indicated. Other studies have also reported that the composition of rice husks consists of mainly cellulose and hemicellulose [9,23].

The thermal decomposition of palm kernel shells also showed two DTG peaks at temperatures of 280 and 370 °C, with the major peak similar to lignin decomposition, suggesting that the palm waste biomass contained more lignin than the other main components. Other studies [33] have reported that palm shell waste is composed of mainly cellulose and lignin. The thermal decomposition of cotton stalks showed two DTG peaks between temperatures of 300 and 350 °C representing the temperature where hemicellulose and cellulose decompose. Other studies [34,35] of the thermal decomposition of cotton stalks suggest a higher content of cellulose compared to hemicellulose and lignin. Coconut shell also showed two DTG thermal decomposition peaks at temperatures of 280 and 360 °C, suggesting a composition of mainly cellulose and hemicellulose.

Fig. 3(a) shows the TGA and Fig. 3(b) shows the DTG thermograms of the mixtures of cellulose, hemicellulose and lignin. In the case of the 50:50 mixture of cellulose and lignin, there was a single DTG peak which occurred between the individual DTG peaks of cellulose and lignin. For the 50:50 mixture of xylan and lignin, two decomposition peaks were observed corresponding to the thermal decomposition of hemicellulose and lignin however, the DTG thermogram peaks appeared to shift to lower decomposition temperatures, indicating interaction between the individual components. The mixture of 50:50 xylan and cellulose exhibited three peaks which corresponded to the two decomposition DTG thermogram peaks of hemicellulose (although shifted to a higher temperature) and the cellulose decomposition DTG peak. A mixture of the three biomass components in equal proportions exhibited two separate DTG peaks, one at a temperature at less than a temperature of 300 °C which may be attributed to the mass loss of xylan while the thermogram DTG peak above 300–400 °C could be the mass loss contribution by cellulose and some lignin.

3.2. Product yield from the pyrolysis and pyrolysis-catalytic steam reforming of biomass wastes

The product yield and gas compositions from the pyrolysis (no catalyst) and pyrolysis-catalytic steam reforming of the agricultural waste biomass samples are shown in Table 4. The table shows the pyrolysis of the biomass wastes in the absence of the catalyst and without steam, but with silica sand in place of the catalyst. The results show that the sugarcane bagasse produced the highest total gas yield of 43.3 wt.%, palm kernel shell and coconut shell produced similar yields of gas at about 42 wt.% while rice husk and cotton stalk produced approximately the same gas yield of 39 wt.%. The highest char yield was produced by rice husk with a value of 37 wt.% and the lowest char production is cotton stalk of about 24 wt.%. Rice husks are known to have a high ash content which would contribute to the char yield.

Introduction of steam and the 10%$NiAl_2O_3$ catalyst to the pyrolysis-catalytic steam reforming process significantly increased total gas yield, with between 13 and 28 wt.% increase in gas yield observed across all the biomass samples. Several experimental investigations have also reported higher total gaseous yield by introducing catalysts compared to absence of catalyst in the pyrolysis-catalytic steam reforming process [9,12,36,37].

Table 4
Mass balance and product yield from the pyrolysis and pyrolysis-catalytic steam reforming of biomass samples.

Feedstock	Rice husk		Coconut shell		Sugarcane		Palm kernel shell		Cotton stalk		Wheat straw	
	Sand	Catalyst	Sand	Catalyst	Sand	Catalyst	Sand	Catalyst	Sand	Catalyst	Sand	Catalyst
Product yield (wt.%)												
Gas	38.71	52.39	41.88	60.70	43.31	61.29	42.00	69.76	39.38	57.39	37.85	50.64
Char	36.50	39.00	26.00	29.00	25.50	25.00	30.00	27.50	24.00	25.00	30.50	30.50
Liquid[a]	24.79	7.11	32.12	7.80	31.19	10.71	28.00	2.74	36.62	17.61	31.65	15.86
Catalyst carbon	–	1.50	–	2.50	–	3.00	–	0.00	–	0.00	–	3.00
Gas composition (vol%)												
CO	31.86	15.70	32.45	19.12	30.14	17.09	30.01	21.79	29.10	18.45	26.79	16.13
H_2	33.58	57.63	31.14	58.21	29.80	59.23	32.88	57.36	34.68	57.95	32.46	54.06
CO_2	20.38	23.99	17.56	20.74	22.50	21.50	19.79	18.49	18.53	21.09	21.48	22.35
CH_4	11.93	2.45	16.37	1.80	14.79	2.06	14.70	2.27	14.95	2.40	15.64	6.92
$C_2{-}C_4$	2.25	0.24	2.47	0.12	2.77	0.12	2.62	0.08	2.74	0.10	3.63	0.55
Gas composition (mmol g^{-1})												
CO	5.84	4.96	6.54	7.26	5.91	6.63	6.04	9.63	5.68	6.60	4.80	4.89
H_2	6.16	18.22	6.28	22.11	5.84	22.96	6.62	25.35	6.77	20.74	5.81	16.38
CO_2	3.74	7.58	3.54	7.88	4.41	8.34	3.98	8.17	3.62	7.55	3.85	6.77
CH_4	2.19	0.77	3.30	0.68	2.90	0.80	2.96	1.00	2.92	0.86	2.80	2.10
$C_2{-}C_4$	0.41	0.07	0.50	0.05	0.54	0.04	0.53	0.04	0.54	0.04	0.65	0.17

[a] By difference.

Table 4 also shows the volumetric gas concentration from pyrolysis (without the addition of steam or catalyst) and also in the presence of steam and the 10%$NiAl_2O_3$ catalyst. Pyrolysis produced a volumetric hydrogen concentration between 30 and 35 vol%, carbon monoxide produced was between 27 and 32 vol% for the different biomass samples. Furthermore, carbon dioxide was between 18 and 23 vol%, methane was between 12 and 16 vol% and $C_2{-}C_4$ hydrocarbon gases were between 2 and 4 vol%.

The introduction of the 10%$NiAl_2O_3$ catalyst and steam to the pyrolysis-catalytic steam reforming process produced a marked increase in hydrogen production. There was a consequent decrease in carbon monoxide and methane produced. In terms of hydrogen yield (mmol g^{-1}) from the mass of biomass feedstock used, the yield was wheat straw < rice husk < cotton stalk < coconut shell < sugarcane < palm kernel shell. The increase in the production of hydrogen resulted in an increase in the volumetric proportion of hydrogen, resulting in an increase in volumetric hydrogen in the product gas to 57.63 vol%, 58.21 vol%, 59.23 vol%, 57.36 vol%, 57.95 vol% and 54.06 vol% for rice husk, coconut shell, sugarcane, palm kernel shell, cotton stalk and wheat straw respectively.

3.3. *Pyrolysis and catalytic-steam reforming of biomass components*

The pyrolysis-catalytic steam reforming of lignin, cellulose, hemicellulose (xylan) and the components mixture was conducted in the two stage fixed bed reactor and the results are shown in Table 5. In the absence of catalyst and steam, cellulose and hemicellulose pyrolysis generated a gas yield of about 50 wt.% and lignin about 30 wt.%. Pyrolysis of lignin marginally generated the highest hydrogen production compared to cellulose and hemicellulose, as also reported by Uddin et al. [38] and Yang et al. [22]. The highest char residue was observed with lignin at ~45 wt.%, while that of cellulose was ~20 wt.% and xylan ~18 wt.%. Since the first stage pyrolysis reactor was operated under the same conditions for the uncatalysed experiments (sand used in stage two) and for the catalysed experiments (catalyst used in stage two), the char residue would be similar for the two sets of experiments. The higher char yield for lignin pyrolysis compared with cellulose and hemicellulose char yield has been reported by others [36].

Table 5
Mass balance and product yield from the pyrolysis and pyrolysis-catalytic steam reforming of biomass components.

	Lignin		Cellulose		Xylan	
	Sand	Catalyst	Sand	Catalyst	Sand	Catalyst
Product yield (wt.%)						
Gas	29.92	50.48	50.71	55.44	49.56	55.45
Char	44.50	44.00	19.00	19.50	15.00	17.50
Liquid[a]	25.58	2.85	30.29	23.06	35.44	24.55
Catalyst carbon	–	2.67	–	2.00	–	2.50
Gas composition (vol%)						
CO	29.38	16.34	43.48	20.69	38.23	18.15
H_2	40.23	64.02	26.48	56.43	28.70	58.77
CO_2	10.06	13.68	15.02	18.69	18.26	21.04
CH_4	18.20	5.84	11.40	3.95	11.61	1.92
$C_2{-}C_4$	2.13	0.12	3.62	0.24	3.20	0.11
Gas composition (mmol g^{-1})						
CO	5.15	6.44	9.94	7.23	8.58	6.34
H_2	7.03	25.25	6.06	19.72	6.44	20.54
CO_2	1.76	5.35	3.44	6.53	4.10	7.35
CH_4	3.20	2.29	2.61	1.38	2.60	0.67
$C_2{-}C_4$	0.31	0.05	0.82	0.08	0.72	0.04

[a] By difference.

Introduction of the 10 wt.% $NiAl_2O_3$ catalyst and steam to the process showed an increase in gas yield for the three biomass components, at 55.45, 55.44 and 50.48 wt.% for cellulose, hemicellulose and lignin respectively. The production of hydrogen from the catalytic steam reforming process was highest for lignin, CO and CO_2 yields for hemicellulose and cellulose were higher compared to lignin. The presence of methoxyl-O-CH_3 containing hydrocarbons in the lignin structure and their release during pyrolysis has been implicated in the enhanced production of H_2 from lignin [22,36]. However, the presence of C–O and C=O structures in cellulose and hemicellulose results in enhanced production of CO and CO_2.

Table 6 shows the influence of different mixtures of the main biomass components on the product yield and composition of gases for the pyrolysis and for the pyrolysis – catalytic steam reforming processes. The pyrolysis catalytic steam reforming of the lignin and xylan mixture (1:1) produced the highest gas yield of 63:19 wt.%. Lignin and xylan (1:1) produced the most char residue at ~36.0 wt.% compared with the cellulose and xylan mixture at ~19.5 wt.%. The mixture of the three biomass components lignin, cellulose and xylan with pyrolysis-catalytic steam reforming produced a gas yield of 59.31 wt.% and a char residue of 26.0 wt.%. The product yield, such as the gas yield and char production, observed for the three biomass components mixture was a reflection of the superposition of the individual components. The calculated value of product yield and gas composition of the different biomass component mixtures was determined based on the proportion of each individual component product yield and gas composition generated by individual biomass components. The gas yield for the experimental data showed a higher value than the calculated value, suggesting some interaction of the components during reaction. For example, the yield of H_2 for the experimental value was lower than the calculated value whereas experimental CO_2 and CH_4 production were higher than the calculated value.

There are several reports in the literature related to interaction of cellulose, hemicellulose and lignin during the pyrolysis process [26]. Some have reported negligible interaction of biomass components. For example Yang et al. [22] using a TGA-FTIR and a packed-bed with micro gas chromatography analytical system suggested negligible interaction of the components. They reported that superposition of the yields and composition of products from the individual biomass components reflected closely the composition of their mixtures [22]. Raveendran et al. [39] also researched the pyrolysis of biomass components using a TGA and also a packed-bed pyrolysis reactor and reported no detectable interaction between the biomass components during pyrolysis.

However, other researchers have demonstrated significant interaction of the main components of biomass during pyrolysis. For example, lignin addition to cellulose has been reported to enhance the product yield of low molecular weight compounds and reduce the yield of char [40]. Also, Liu et al. [26] reported significant interaction of biomass components, particularly between lignin - hemicellulose and hemicellulose - cellulose. For example, they reported that lignin addition to hemicellulose decreased the yield of 2-furaldehyde and other aldehydes and ketones, and hemicellulose addition to cellulose decreased the yield of levoglucosan and increased the formation of hydroxyacetaldehyde.

However, it has also been concluded from a review of the composition of the products obtained from the pyrolysis of biomass, cellulose, hemicelluloses and lignin that the process operating conditions, such as heating rate, reactor temperature, particle size and gas residence time may have a more significant influence on the yield and composition of products [41].

3.4. Hydrogen production in terms of lignin content

Table 7 shows the results of experiments to verify the effect of lignin content from the pyrolysis of various biomass component mixtures. The percentage of lignin was varied from 10, 50, 90 and 100 wt.% with a balance of equal quantities of cellulose and hemicellulose. The highest gas yield (40.66 wt.%) was obtained at the lowest lignin content of 10 wt.%, reflecting the higher gas yield from cellulose and hemicellulose. It was observed that as lignin content was increased, H_2 production increased and CO and CO_2 decreased. Burhenne et al [27] studied the effect of biomass components in a fixed bed reactor and in a TGA with the observation that lignin content was the main controlling factor in relation to thermal decomposition temperatures and product yield. They also suggested that a high lignin content leads to higher yield of solid residue, lower product gas yield and a higher devolatilization temperature as compare to cellulose and hemicellulose. Zheng et al. [42], reported the role of lignin as the cementing medium of biomass via cross-linking between cellulose and hemicellulose

Table 6
Product yield and gas composition from pyrolysis and pyrolysis-catalytic steam reforming of mixtures of biomass components.

	Lignin + Cellulose (1:1)		Lignin + Xylan (1:1)		Cellulose + Xylan (1:1)		Lignin + Cellulose + Xylan (1:1:1)	
	Sand	Catalyst	Sand	Catalyst	Sand	Catalyst	Sand	Catalyst
Product yield (wt.%)								
Gas yield	42.21	63.19	34.45	53.54	49.82	61.48	40.40	59.31
Char	30.50	29.50	35.50	36.50	19.00	20.00	28.50	26.00
Liquid[a]	27.29	5.81	30.05	7.96	31.18	16.52	31.1	12.19
Catalyst carbon	–	1.50	–	2.00	–	2.00	–	2.50
Gas composition (vol%)								
CO	37.10	18.02	29.14	13.86	39.20	17.74	32.94	16.29
H_2	29.65	55.51	32.77	56.13	27.42	55.58	31.58	53.69
CO_2	14.23	20.00	20.60	22.99	18.54	24.63	19.13	23.28
CH_4	15.81	6.18	15.57	6.56	11.74	1.87	13.86	6.30
$C_2–C_4$	3.20	0.29	1.93	0.46	3.10	0.18	2.49	0.45
Gas composition (mmol g^{-1})								
CO	7.57	7.10	4.80	4.55	8.70	6.31	6.28	5.67
H_2	6.05	21.86	5.39	18.42	6.09	19.78	6.02	18.70
CO_2	2.90	7.88	3.39	7.54	4.12	8.76	3.64	8.11
CH_4	3.23	2.44	2.56	2.15	2.61	0.66	2.64	2.19
$C_2–C_4$	0.65	0.11	0.32	0.15	0.69	0.06	0.47	0.16

[a] By difference.

Table 7
Product yield and gas composition from the pyrolysis of different mixtures of lignin with cellulose/hemicellulose.

Pyrolysis	10 wt.% Lignin 45 wt.% Cellulose 45 wt.% Hemicellulose	50 wt.% Lignin 25 wt.% Cellulose 25 wt.% Hemicellulose	90 wt.% Lignin 5 wt.% Cellulose 5 wt.% Hemicellulose	100 wt.% Lignin
Gas yield (wt.%)	40.66	38.97	33.56	29.92
Char (wt.%)	25.00	32.50	41.00	44.50
Gas composition (vol%)				
CO	34.90	32.37	30.47	29.38
H_2	29.93	32.02	35.99	40.23
CO_2	20.19	18.09	14.05	10.06
CH_4	12.54	14.99	17.49	18.20
C_2–C_4	2.43	2.53	2.01	2.13
Gas composition (mmol g^{-1})				
CO	6.46	6.07	5.44	5.15
H_2	5.54	6.00	6.42	7.03
CO_2	3.74	3.39	2.51	1.76
CH_4	2.32	2.81	3.12	3.20
C_2–C_4	0.45	0.48	0.36	0.31

resulting in a firm mechanical three-dimensional structure of the plant cell wall. Thereby, the higher the lignin content, the higher the resistance of the biomass to degradation and consequently, higher char residue yield instead of gases and volatiles yield.

Table 8 shows the effect of lignin content with a balance of equal quantities of cellulose and hemicellulose and at 10, 50, 90 and 100 wt.% lignin for the pyrolysis-catalytic steam reforming process in the presence of the 10%$NiAl_2O_3$ catalyst. The presence of the 10 wt.% $NiAl_2O_3$ catalyst produced an increase in gas yield and in particular enhanced H_2 yield. Increasing lignin content produced an increasing total gas yield from 55.31 wt.% at 10 wt.% lignin to 64.36 wt.% at 100 wt.% lignin. In addition, higher hydrogen yield was produced with increased lignin content, rising from 14.99 mmol g^{-1} at 10 wt.% lignin content to 28.19 mmol g^{-1} at 100 wt.% lignin content.

3.5. *Analysis of gases produced from lignin in relation to temperature and time*

In a separate experiment and using a different experimental procedure, the gas composition evolved at specific temperatures throughout the pyrolysis process and the pyrolysis-catalytic steam reforming process for 100 wt.% lignin was investigated. Rather than collecting the evolved gases as a total gas yield in the gas sample bag, instead, several gas sample syringes were used to collect the gases as the pyrolysis reactor was heated to 150 °C, then gas samples were collected at every 50 °C temperature increment until the required pyrolysis end temperature of 550 °C was reached. In addition, further gas samples were collected every 5 min at the pyrolysis temperature of 550 °C. For these experiments, in the case of pyrolysis, sand was used in the second stage reactor and for the catalyst experiment, the second stage contained the 10%$NiAl_2O_3$ catalyst maintained at 750 °C and where steam was introduced. The results are shown in Fig. 4. The results show that the composition of each of the product gases, CO, H_2, CO_2, CH_4, and C_2–C_4, increases as the biomass feedstock undergoes pyrolysis or pyrolysis-catalytic steam reforming. The evolution of gases decreases as the thermal degradation of the biomass progresses and complete thermal degradation occurs, leaving the residual char. The highest yield of gases were released at 350 °C for the pyrolysis of lignin while for pyrolysis-catalytic steam reforming of lignin with the 10 wt % $NiAl_2O_3$ catalyst, gas yield peaked between the temperatures of 250–300 °C indicating a lower decomposition temperature for the lignin in the presence of the 10%$NiAl_2O_3$ catalyst.

There have been several reports on the mechanism for the catalytic steam reforming of biomass pyrolysis gases in order to understand the formation of CO and H_2. For example, Guan et al. [43] have reviewed the catalytic steam reforming process for biomass tar, which is analogous to the catalytic steam reforming of the range of hydrocarbons produced during biomass pyrolysis. They suggest a mechanism where larger molecular weight hydrocarbons undergo several reactions including thermally and catalytic cracking, reforming (with CO_2 or

Table 8
Product yield and gas composition for different mixtures of lignin with cellulose/hemicellulose from the pyrolysis-catalytic steam reforming of biomass components.

Catalytic steam reforming	10 wt.% Lignin 45 wt.% Cellulose 45 wt.% Hemicellulose	50 wt.% Lignin 25 wt.% Cellulose 25 wt.% Hemicellulose	90 wt.% Lignin 5 wt.% Cellulose 5 wt.% Hemicellulose	100 wt.% Lignin
Gas yield (wt.%)	55.31	56.04	58.04	64.38
Char (wt.%)	24.00	32.50	40.50	43.50
Catalyst carbon (wt.%)	1.50	1.50	1.50	2.50
Gas composition (vol%)				
CO	20.00	18.19	15.74	15.33
H_2	49.31	52.46	56.69	62.18
CO_2	23.44	21.62	20.09	18.02
CH_2	6.31	7.20	7.21	4.42
C_2–C_2	0.94	0.54	0.27	0.06
Gas composition (mmol g^{-1})				
CO	6.08	6.01	5.85	6.95
H_2	14.99	17.32	21.06	28.19
CO_2	7.13	7.14	7.46	8.17
CH_4	1.92	2.38	2.68	2.00
C_2–C_4	0.29	0.18	0.10	0.02

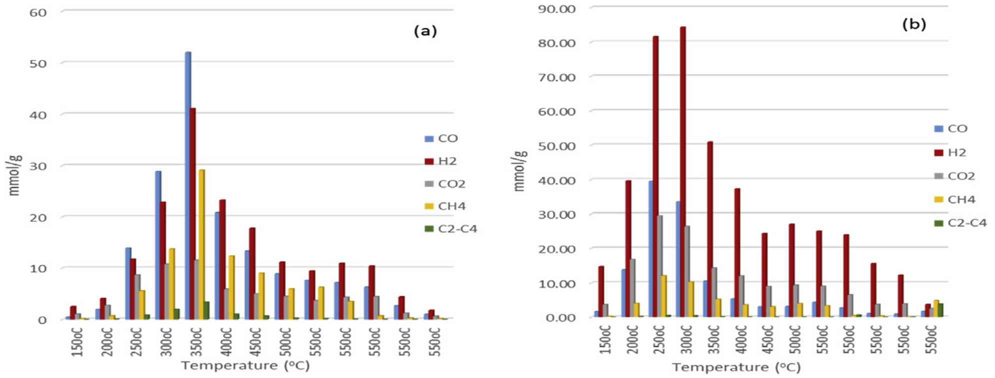

Fig. 4. Evolution of gases from (a) pyrolysis and (b) catalytic steam reforming of lignin in relation to temperature and corresponding time.

H_2O), water gas shift, etc on the catalyst to produce mainly CO and H_2. In addition, coke formation can occur on the catalyst due to larger molecular weight hydrocarbon polymerisation reactions. Su et al. [44] have further elucidated the catalytic steam reforming mechanism and have suggested that the hydrocarbons interact with the catalyst metals by dissociation and adsorption on the catalyst surface followed by metal-catalysed dehydrogenation. Water at the catalyst surface hydroxylates and the formed OH radicals migrate to the metal sites and oxidise the hydrocarbon intermediate fragments to form the CO and H_2.

4. Conclusions

The investigation carried out in this study has involved the pyrolysis and the pyrolysis-catalytic steam reforming of six different biomass samples namely: rice husk, coconut shell, sugarcane, palm kernel shell, cotton stalk and wheat straw. In addition, the pyrolysis and pyrolysis-catalytic steam reforming of the three main biomass components, cellulose, xylan and lignin were also investigated. The influence on the different types of biomass and the main biomass components on product yield and product gas composition, in particular hydrogen, was investigated. The results showed that introduction of steam and catalyst into the pyrolysis-catalytic steam reforming process significantly increased gas yield as well as product syngas hydrogen composition. Hydrogen yield from pyrolysis of the biomass types ranged from 5.81 mmol g^{-1} for wheat straw to 6.77 mmol g^{-1} for cotton stalks. For pyrolysis-catalytic steam reforming, the hydrogen yield ranged from 16.38 mmol g^{-1} for wheat straw to 25.35 mmol g^{-1} for palm shell kernals. For pyrolysis of the biomass components, lignin produced the highest yield of hydrogen, whereas cellulose and hemicellulose favoured CO and CO_2 production, which was linked to the differences in chemical structure of lignin compared to cellulose and hemicellulose. It was also observed that by increasing the lignin content in mixtures of the biomass components, the hydrogen yield increased, suggesting that the lignin component of biomass sample is the main controlling factor for hydrogen yield.

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Appendix A. Supplementary data

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